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DESCRIPTION

METHOD OF FORMING AN ELECTROCOATING FILM, ELECTROCOATING
FILM, AND ELECTRODEPOSITED ARTICLE

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TECHNICAL FIELD

The present invention relates to a method of forming an electrocoating film, an electrocoating film, and an electrodeposited article.

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BACKGROUND TECHNOLOGY

Recently attempts have been made to form an insulating coating film from a coating on a metallic surface.

Regarding the substrate of a multi-layer printed wiring board, for instance, a metallic substrate formed with an epoxy resin insulating layer on which an electric circuit is formed by electroless plating for improved heat dissipation, called a metal core PWB, has so far been developed (e.g. Itoh, Kinji: Introduction to Manufacture of Printed Wiring Boards for Certification of Printed Wiring Board Engineers, 1st Edition, July 6, 2001, pp.67-69).

However, the recent trend toward higher-integration and higher-density substrate boards presents with the problem of leaks between the metal substrate and the circuit due to the minute pinholes existing in the insulating layer and, therefore, this insulating layer is required to have high dielectric properties.

Electrocoating compositions have excellent throwing powers and yield comparatively even coats regardless of the shape of work as well as sufficient dielectric properties so that attempts have been made to form insulating layers using electrocoating compositions. Although such attempts are rewarded with several advantages of electrocoating, this electrocoating film is usually not so flat and smooth as desired and tends to develop pinholes owing to evolution

of hydrogen gas in the electrodepositing process, thus making it difficult to implement a high-level dielectric property using an electrocoating composition.

5 SUMMARY OF THE PRESENT INVENTION

The present invention has for its object to provide a method of forming an electrocoating film having an excellent smoothness and exceptionally high dielectric properties with a drastically reduced incidence of pinhole
10 formation, such an electrocoating film, and such an electrodeposited article.

The present invention is first directed to a method of forming an electrocoating film comprising coating a work with an electrocoating composition curable by heating and
15 irradiation with an activation energy beam

in which an electrodepositing step, an aqueous cleaning step, a pre-baking step, an activation energy beam irradiation step, and a post-baking step are serially carried out in the order mentioned.

20 The activation energy beam irradiation step may be carried out directly following said pre-baking step without cooling the work.

The heating in the above post-baking step may be continuous from the pre-baking step.

25 Preferably, the electrocoating composition comprises a resin composition containing sulfonium and propargyl groups.

Preferably, the electrocoating composition is a cationic electrocoating composition.

30 The present invention is further directed to an electrocoating film

which is formed by the above method of forming an electrocoating film.

In addition, the present invention is directed to an
35 electrodeposited article having the electrocoating film.

The present invention is further directed to a method of forming a multilayer film

in which the above electrocoating film is further coated with an overcoat.

5 The present invention is further directed to a multilayer film

which is formed by the method of forming a multilayer film.

10 Furthermore, the present invention is directed to an article having the multilayer film.

DISCLOSURE OF INVENTION

The method of forming an electrocoating film according to the present invention is a method of forming
15 an electrocoating film which comprises coating a work with an electrocoating composition curable by heating and irradiation with an activation energy beam, and comprises an electrodepositing step, an aqueous cleaning step, a pre-baking step, an activation energy beam irradiation step,
20 and a post-baking step.

The electrocoating composition mentioned above contains a binder component curable by heating and irradiation with an activation energy beam in addition to the ionic groups necessary for electrodeposition. The
25 binder component may be a component having a functional group curable by heating and irradiation with an activation energy beam or one having both a heat-curable functional group and an activation energy beam-curable functional group, and whichever of these can be employed.

30 The curability by irradiation with an activation energy beam, as referred to above, includes not only the mode in which a curing reaction is directly caused by an activation energy beam itself but also the mode in which a curing reaction is caused by the active species generated
35 by an activation energy beam. The activation energy beam-

curable functional group may include an unsaturated bond, such as a double bond or a triple bond, a combination of the above unsaturated bond and a thiol group, an epoxy group, a maleimide group, an oxetane group, an alkoxysilyl group and so on, but in consideration of the stability of coexistence with other functional groups, either an unsaturated bond or a combination of the above unsaturated bond and a thiol group is preferred. Moreover, said unsaturated bond is not only curable by irradiation with an activation energy beam but may be converted to a heat-curable functional group by formulating a heat-sensitive radical initiator, such as an dialkyl peroxide, peroxy-carboxylic acid, peroxy-carbonate, peroxy-ester, hydroperoxide, ketone peroxide, azodinitrile or benzopinacol silyl ether, in the coating.

Further, as the heat-curable functional group, those functional groups which are well known in the coating art can be utilized. The functional group mentioned above is not particularly restricted unless it directly reacts with said ionic group necessary for electrodeposition or said activation energy beam-curable functional group or interferes with the electrodepositing process or the curing by an activation energy beam. Specifically, the preferred one is hydroxyl group. As regards this functional group capable of curing on exposure to heat, a curing agent serving as a partner in the curing reaction is usually incorporated in the coating composition. In the case where the functional group capable of curing on exposure to heat is hydroxyl, the curing agent which can be used may be any of those well known in the art, such as an optionally blocked polyisocyanate or melamine resin, for instance.

For example, Japanese Kokai Publication Hei-05-263026 discloses a UV-curable cationic electrocoating composition comprising 10 to 70 parts by weight of a polyfunctional acrylate having three or more acryloyl groups within the

molecule and 30 to 90 parts by weight of a resin suitable for cationic electrodeposition and having an average molecular weight of 2000 to 30000 as active components. Such electrocoating compositions containing a binder component having an unsaturated bond as an activation energy beam-curable functional group are known and, therefore, by incorporating a heat-sensitive radical initiator in such a known coating, there can be provided an electrocoating composition for use in the method of forming an electrocoating film according to the present invention. Furthermore, it is not difficult for those skilled in the art to provide an electrocoating composition for use in the method of forming an electrocoating film by introducing a heat-curable functional group into a binder component having said unsaturated bond as an activation energy beam-curable functional group and selecting a curing agent compatible therewith.

Furthermore, an aqueous dispersion comprising a cationic group-containing polyurethane (meth)acrylate having an ethylenically unsaturated terminal (meth)acryloyl double bond and a reactive diluent having at least two ethylenically unsaturated (meth)acryloyl double bonds as a binder component and a light-sensitive radical initiator and/or a heat-sensitive radical initiator, which is disclosed in Japanese Kohyo Publication 2002-531676, can be used as the electrocoating composition for use in the method of forming an electrocoating film according to the present invention. Here, the (meth)acryloyl double bond in said aqueous dispersion has a bromine value equal to 20 to 150 g bromine/100 g solids and the terminal (meth)acryloyl double bond of ethylenic unsaturation from said polyurethane (meth)acrylate is bound to a cationic group-containing polyurethane prepolymer through a urethane, urea, amide or ester group.

Furthermore, a cationic electrocoating composition

containing sulfonium and propargyl groups is disclosed in WO 98/03595. This electrocoating composition, too, can be used in the method of forming an electrocoating film according to the present invention. The sulfonium group
5 content of this electrocoating composition per 100 g of resin solids is 5 to 400 millimoles and the propargyl group content on the same basis is 10 to 495 millimoles, the total content of sulfonium and propargyl groups being not greater than 500 millimoles. Furthermore, a component
10 containing a double bond as unsaturation in addition to propargyl group may also be used in combination. Incidentally, it is known that said cationic electrocoating composition containing sulfonium and propargyl groups undergoes curing when heated even in the absence of the
15 heat-sensitive radical initiator. Moreover, because it contains the propargyl group being an unsaturated bond, the coating can be cured by irradiation with an activation energy beam.

The electrocoating composition for use in the method
20 of forming an electrocoating film according to the present invention may be whichever of an anionic electrocoating composition and a cationic electrocoating composition but is preferably a cationic electrocoating composition in view of the release of ions from the work.

25 From the standpoint of dielectric property of the formed electrocoating film, the electrocoating composition for use in the method of forming an electrocoating film according to the present invention is preferably said cationic electrocoating composition containing sulfonium
30 and propargyl groups. As such cationic electrocoating composition, there can be mentioned Insuleed Series (electrolytically active electrocoatings, manufactured by Nippon Paint Co.)

Where necessary, the electrocoating composition for
35 use in the method of forming an electrocoating film

according to the present invention may contain a light-sensitive radical initiator. As the light-sensitive radical initiator which can be comprised in said electrocoating composition, various compounds which are well known to those skilled in the art can be employed. Among such substances are benzoin compounds such as benzoin, benzoin isopropyl ether, benzoin isobutyl ether, and so on; benzophenone compounds such as benzophenone, 4,4'-bis(dimethylamino)benzophenone (Michler's ketone), and so on; xanthone compounds such as xanthone, thioxanthone, and so on; acetophenone compounds such as 2-phenyl-2-hydroxyacetophenone, α,α -dichloro-4-phenoxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2,2-diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-hydroxy-2-methylpropiofenone, 2,2-dimethoxy-2-phenylacetophenone (benzyl dimethyl ketal), and so on; ethyl 4-dimethylaminobenzoate, 4,4'-diazidostilbene-2,2'-disulfonic acid, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, and so forth. These light-sensitive radical initiators are usually formulated in a proportion of 0.1 to 10 % by weight based on the resin solids of the coating composition.

The electrocoating composition for use in the method of forming an electrocoating film according to the present invention may contain those pigments and additives which are conventionally formulated in electrocoating compositions.

The work for use in the method of forming an electrocoating film according to the present invention is not particularly restricted provided that the area to be coated is electrically conductive. There is no restriction on the shape of the work.

The electrodepositing step in the method of forming an electrocoating film according to the present invention comprises electrodepositing an electrically conductive work with the above-described electrocoating composition to give

an uncured electrodeposited coat. The relevant electrodepositing conditions such as electrodepositing bath temperature, electrodepositing voltage and current time are established according to the particular electrocoating composition to be used but are preferably so set as to yield a dry film thickness of 5 to 30 μm .

The aqueous cleaning step in the method of forming an electrocoating film according to the present invention, which is carried out on completion of said electrodepositing step, comprises washing off the superfluous electrocoating composition remaining on the work and electrodeposited coat. The solvent for use in this aqueous cleaning step is preferably deionized water from the standpoint of dielectric property of the resulting electrocoating film but there may optionally be used a two-stage method which comprises prewashing with a mixture solvent of deionized water and a water-soluble carboxylic acid compound, such as acetic acid, lactic acid or the like, and postwashing with deionized water. The residual electrocoating composition can be thereby removed more effectively.

The mode of the above aqueous cleaning is not particularly restricted but any of those techniques which are well known in the art, such as dipping and spraying, can be employed. The cleaning time is not particularly restricted but may, for example, be 30 seconds to 2 minutes.

The pre-baking step which is carried out on completion of said aqueous cleaning step in the method of forming an electrocoating film according to the present invention is not intended to cure the whole of said electrodeposited coat but intended to melt and let flow the uncured electrodeposited coat once formed to thereby eliminate film defects such as pinholes for improved evenness and surface smoothness of the coat. Therefore, even in the case where the heating is further continued,

this step is regarded as having been completed at the time-point where the electrodeposited coat has been molten and let flow. The melting and letting-flow of the uncured electrodeposited coat in the above manner is advantageous in that an improvement in the smoothness of the coat as well as elimination of pinholes in the coat can be accomplished to insure a high degree of dielectric property.

Furthermore, improving the smoothness of the coat in this way enables the use of the obtained film in an electric circuit utilizing high-frequency signal. This is because a reduced coarseness of the coat leads to a reduction in the disturbance of the magnetic field by a current so that the product can be made adaptable to high-frequency current applications which are apt to be influenced by a magnetic field. Moreover, the improved surface smoothness can reduce the risk for disconnection of a conductor locating on an electrodeposited article and enables fine-lined conversion of the electrodeposited article on its patterning as well.

The heating temperature for use in the above pre-baking step should, of necessity, be not lower than the temperature causing the electrodeposited coat to melt and it can be judiciously selected according to the kind of electrocoating composition used but is generally within the range of 60 to 130°C. If it is below 60°C, the flow of the uncured electrodeposited coat on melting tends to be insufficient so that pinholes may remain after this step and the evenness or the surface smoothness of the coat may be insufficient. On the other hand, if the temperature exceeds 130°C, the uncured electrodeposited coat may begin to cure before the coat has flown sufficiently, with the consequence that, after this step, pinholes may remain, the evenness of the coat be inadequate, or the surface smoothness of the coat be insufficient. The preferred range is 70 to 110°C. The heating time in said pre-baking

step is not particularly restricted but from coat meltability and industrial points of view, it may for example be 2 to 30 minutes.

5 The activation energy beam irradiation step in the method of forming an electrocoating film according to the present invention, which precedes the post-baking step, is intended to fix the coat surface which has been improved in evenness and smoothness by said pre-baking step. By carrying out this step, the reflow of the electrodeposited
10 coat is inhibited so that even when the electrodeposited coat is further heated and caused to cure thoroughly, the ultimate electrocoating film can be obtained with the high surface smoothness achieved in this step being successfully retained.

15 The activation energy beam which can be used includes ultraviolet light, X-rays, an electron beam, near-infrared light and visible light. The activation energy beam in the context of the present invention does not include heat-generating energy beams such as infrared light, high-
20 frequency waves and microwaves. However, although near-infrared light is a heat-generating energy beam, it is included in said activation energy beam because there exist light-sensitive radical initiators showing initiating functions in this wavelength region.

25 For irradiation with ultraviolet light, there can be used a variety of light sources, such as a mercury arc lamp, a xenon arc lamp, a fluorescent lamp, a carbon arc lamp, a tungsten-halogen copier lamp, and so forth. On the other hand, as emission sources of an electron beam, there can be
30 used electron beam generators such as Cockcroft type, Cockcroft-Walton type, van de Graaff type, resonance transformer type, transformer type, insulating core transformer type, Dynamitron type, linear filament type, high-frequency type, and other devices. It should be
35 understood that when an electron beam is used, it is not

always necessary to use a light-sensitive radical initiator.

The conditions of said irradiation with an activation energy beam in this step vary with the amount of unsaturation in the resin and the molecular weight of the resin in the electrocoating composition used but taking ultraviolet light as an example of said activation energy beam, its wavelength range may be 200 to 500 nm and the integrating radiation dosage may for example be 100 to 10000 mJ/cm² when the coating used contains a light-sensitive radical initiator or 1000 to 20000 mJ/cm² when the coating does not contain a light-sensitive radical initiator. When the integrating radiation dosage is insufficient, fixing of the electrodeposited coat surface is inadequate so that the ultimate electrocoating film tends to be deficient in smoothness. An excessive integrating radiation dosage would not cause any serious trouble but lead to a waste of energy. On the other hand, when an electron beam is used, it is advantageous to carry out the irradiation using an electron beam generator with an output energy of 50 to 500 keV for a predetermined time.

It is also recommendable to adjust the distance between the electrodeposited coat and the light source according to the shape of the work so as to provide for a uniform irradiation with the activation energy beam and bring said integrating radiation dosage and energy into a predetermined range.

The above activation energy beam irradiation step may be carried out directly following said pre-baking step without cooling the work between the steps.

The post-baking step in the method of forming an electrocoating film according to the present invention is intended to thermally cure the electrodeposited coat having a fixed surface following the activation energy beam irradiation step. By carrying out this step, the entirety of the electrodeposited coat inclusive of its interior can

be caused to cure thoroughly. Although the electrodeposited coat undergoes remelting to flow in this step, the coat surface which has been hardened in the preceding step does not melt so that an ultimately cured electrocoating film can be produced with the high surface smoothness obtained in the preceding step being fully retained.

The heating conditions for use in this post-baking step are not particularly restricted provided that the electrocoating film having a fixed surface obtained after said pre-baking step and subsequent activation energy beam irradiation step can be thoroughly cured down to its interior. The above heating conditions can be appropriately established according to the kind of electrocoating composition used and, for example, the heating temperature may be 130 to 260°C. The heating time in this post-baking step is not particularly restricted, either, and may for example be 10 to 30 minutes.

The heating in this post-baking step may be a continuation of the heating in said pre-baking step.

The method of forming an electrocoating film according to the present invention is applicable to electrically conductive substrates and can be used to form electrocoating films on various metallic materials such as copper, iron, galvanized steel sheet, aluminum and so forth.

The electrocoating film of the present invention is formed by the above-described method of forming an electrocoating film, and having such a film, the electrodeposited article of the present invention features very satisfactory dielectric properties and surface smoothness.

The method of forming a multilayer film according to the present invention may comprise applying an overcoat in superimposition on the cured electrocoating film described above. The overcoat is intended to protect and impart an

attractive appearance to said electrocoating film or adding new functions to the multilayer film. The overcoat mentioned just above is not particularly restricted but includes, for example, those materials which can be caused to undergo a curing reaction by heating and/or irradiation with an activation energy beam. Among specific examples are those binders, among the binder components mentioned in the foregoing description of the electrocoating composition of the present invention, which can be cured by heating and/or irradiation with an activation energy beam. In the case of a non-aqueous one, the binder need not have an ionic group. As the skeleton of the binder component, there can be used an acrylic resin, polyester resin, epoxy resin, urethane resin, or the like and where flexibility is further required, these resins may have been modified by introducing a butadiene skeleton, siloxane skeleton or long-chain aliphatic skeleton.

In the case where the overcoat is heat-curable but cannot be cured in the presence of said binder component alone, a curing agent suited to the kind of said reactive functional group can be used as an auxiliary binder component. The curing agent mentioned just above includes amino resins and optionally blocked polyisocyanates.

In addition to said binder component or components, the above overcoat may contain a pigment, a resin particle, and various additives. For imparting electrical conductivity as a new function to the multilayer film, the above overcoat may be supplemented with a metal particle, carbon, metal oxide, and/or the like. For imparting high dielectric properties, glass fiber, ceramics, and so on may be formulated.

The coating method is not particularly restricted but includes the techniques well known to those skilled in the art, such as bar coating, die coating, spray coating, rotary atomizer coating, spin coating, and so forth. By

curing the resulting film by heating and/or irradiation with an activation energy beam, an overcoat can be constructed. The heating conditions and the conditions of activation energy beam irradiation can be judiciously established according to the kind of overcoat used. The cured thickness of the above overcoat is not particularly restricted but may, for example, be 10 to 100 μm .

The application of the overcoat may be carried out in a few divided cycles.

The multilayer film of the present invention is the film obtained by the above-described method of forming a multilayer film, and the article according to this invention has said multilayer film and, therefore, features a high degree of smoothness.

BEST MODE FOR CARRYING OUT THE PRESENT INVENTION

The following examples are intended to illustrate the present invention in further detail without defining the scope of the present invention. In the examples, "part(s)" means "part(s) by weight" unless otherwise specified.

Example 1

Using Insuleed 1004 (product of Nippon Paint Co., an electrolytically active electrocoating, melting temperature 90°C, curing temperature 180°C), a copper substrate (10 cm x 10 cm x 700 μm thick) was electrodeposited at an electrodepositing voltage of 200 V for 1 minute in a dry film thickness of 20 μm to give an uncured electrodeposited coat. The temperature of the electrodepositing bath was 30°C. After electrodepositing, the substrate was cleaned by dipping it in deionized water for 1 minute to remove the superfluous electrocoating composition on the substrate and electrodeposited coat.

Then, the substrate carrying this uncured electrodeposited coat was pre-baked in a heating oven at a set temperature of 90°C for 10 minutes. After completion

of this pre-baking, the substrate was taken out from the oven and the electrodeposited coat on the substrate surface was visually examined. It was found that the coat had flown sufficiently to become smooth.

5 Then, using a high-pressure mercury-vapor lamp (peak wavelength 365 nm, irradiation intensity $50 \text{ mJ}/(\text{cm}^2 \cdot \text{s})$), the substrate was irradiated with ultraviolet light at an integrating radiation dosage of $10000 \text{ mJ}/\text{cm}^2$.

10 Thereafter, the substrate was post-baked in a heating oven at a set temperature of 180°C for 20 minutes to give an electrocoating film.

Example 2

15 A substrate having an uncured electrodeposited coat as obtained in the same manner as in Example 1 was used as the work. Meanwhile, a device capable of effecting both heating and UV irradiation was set to a heating temperature of 90°C and, for UV irradiation, to a peak wavelength of 365 nm, an irradiation intensity of $50 \text{ mJ}/(\text{cm}^2 \cdot \text{s})$ and an
20 integrating radiation dosage of $10000 \text{ mJ}/\text{cm}^2$. Using the above device, heating alone was carried out for 9 minutes. Then, with the heating being further continued under the same conditions as above for 1 minute, the work was irradiated with UV light for 1 minute.

25 Thereafter, the work was caused to cure by the post-baking in a heating oven set to 180°C for 20 minutes to give an electrocoating film.

Example 3

30 Using CCR-232GF (product of Asahi Chemical Research Co., an epoxy resin overcoat), the electrocoating film obtained in Example 2 was spray-coated in a cured thickness of $25 \mu\text{m}$. Then the work was cured by heating at 150°C for 60 minutes to give a multilayer film.

Example 4

Using a coating material prepared by adding 1 part of Irgacure 651 (benzyl dimethyl ketal, product of Chiba-Geigy, a light-sensitive radical initiator) to 100 parts resin solids of Insuleed 1004 in lieu of Insuleed 1004, the procedure of Example 1 was otherwise faithfully followed to give an uncured electrodeposited coat which had flowed sufficiently to present with a smooth surface.

Then, except that the integrating radiation dosage of a high-pressure mercury vapor lamp was set to 200 mJ/cm², the work was post-baked in the same manner as in Example 1 to give an electrocoating film.

Comparative Example 1

Omitting the pre-baking and UV irradiation steps, the procedure of Example 1 was otherwise faithfully followed to give an electrocoating film.

Comparative Example 2

Omitting the pre-baking step, the procedure of Example 1 was otherwise faithfully followed to give an electrocoating film.

Comparative Example 3

Omitting the UV irradiation step, the procedure of Example 1 was otherwise faithfully followed to give an electrocoating film.

<Evaluation Tests>

Smoothness

Using SJ-201 (the surface roughness tester manufactured by Mitsutoyo Co.), the surface roughness Ra values of the electrocoating films obtained in Examples 1, 2 and 4 and in Comparative Examples 1-3 and the corresponding value of the multilayer film obtained in

Example 3 were respectively measured. As measuring conditions, a cutoff point of 0.8 mm was used. The results are presented in Table 1.

5 Dielectric breakdown voltage

The dielectric breakdown voltage values of the electrocoating films obtained in Examples 1, 2 and 4 and Comparative Examples 1 to 3 and the corresponding value of the multilayer film obtained in Example 3 were respectively
 10 measured with Auto Tester Model 8525 (the breakdown voltage tester manufactured by Tsuruga Electric Co.). The results are presented in Table 1.

Table 1

	Example				Comparative Example		
	1	2	3	4	1	2	3
Smoothness (μm)	0.15	0.22	0.20	0.16	0.35	0.67	0.35
Dielectric property (KV)	4.6	4.9	7.5	4.4	2.5	0.8	2.7

15

It will be apparent from Table 1 that the electrocoating films (Examples 1, 2 and 4) obtained by the method of forming an electrocoating film according to the present invention and the multilayer film (Example 3)
 20 obtained by the method of forming a multilayer film according to the present invention are outstanding in smoothness and dielectric properties. However, the film obtained by omitting the pre-baking step (Comparative Example 2), the film obtained by omitting the pre-baking
 25 and activation energy beam irradiation steps (Comparative Example 1) and the film obtained by omitting the activation energy beam irradiation steps (Comparative Example 3) were inferior in surface smoothness and dielectric properties.

INDUSTRIAL APPLICABILITY

The method of forming an electrocoating film according to the present invention comprises a pre-baking step and an activation energy beam irradiation step which
5 are carried out in that order prior to a post-baking step, with the result that the resulting electrocoating film is outstanding in surface smoothness and dielectric properties.

Moreover, the method of forming a multilayer film according to the present invention comprises applying an
10 overcoat in superimposition on the electrocoating film obtained by said method of forming an electrocoating film and the resulting multilayer film is also outstanding in surface smoothness and dielectric properties.

The underlying principle of these methods is that the
15 surface roughness of the uncured coat formed by electrodepositing and the pinholes existing in the coat can be reduced or eliminated by the pre-baking step which causes the uncured electrodeposited coat to melt and flow, thus providing for evenness and smoothness, the film
20 surface is then fixed to preserve said evenness and smoothness by irradiation with an activation energy beam and, thereafter, the entirety of the coat is cured by post-baking.

The method of forming an electrocoating film
25 according to the present invention and the method of forming a multilayer film according to the present invention provide an electrocoating film and a multilayer film, both having every satisfactory surface smoothness and dielectric properties and, thus, finding application in
30 various kinds of electronic and electric equipment.

CLAIMS

1. A method of forming an electrocoating film comprising coating a work with an electrocoating
5 composition curable by heating and irradiation with an activation energy beam

in which an electrodepositing step, an aqueous cleaning step, a pre-baking step, an activation energy beam irradiation step, and a post-baking step are serially
10 carried out in the order mentioned.

2. The method of forming an electrocoating film according to Claim 1,

wherein said activation energy beam irradiation step
15 is carried out directly following said pre-baking step without cooling the work.

3. The method of forming an electrocoating film according to Claim 1 or 2,

20 wherein the heating in said post-baking step is continuous from said pre-baking step.

4. The method of forming an electrocoating film according to any of Claims 1 to 3,

25 wherein said electrocoating composition comprises a resin composition containing sulfonium and propargyl groups.

5. The method of forming an electrocoating film according to any of Claims 1 to 4,

30 wherein said electrocoating composition is a cationic electrocoating composition.

6. An electrocoating film

which is formed by the method of forming an
35 electrocoating film according to any of Claims 1 to 5.

7. An electrodeposited article having the electrocoating film according to Claim 6.

5 8. A method of forming a multilayer film
 in which the electrocoating film according to Claim 6
 is further coated with an overcoat.

 9. A multilayer film
10 which is formed by the method of forming a multilayer
 film according to Claim 8.

 10. An article having the multilayer film according
 to Claim 9.
15

ABSTRACT

The present invention has for its object to provide a method of forming an electrocoating film having an
5 excellent smoothness and exceptionally high dielectric properties with a drastically reduced incidence of pinhole formation, such an electrocoating film, and such an electrodeposited article.

A method of forming an electrocoating film comprising
10 coating a work with an electrocoating composition curable by heating and irradiation with an activation energy beam in which an electrodepositing step, an aqueous cleaning step, a pre-baking step, an activation energy beam
irradiation step, and a post-baking step are serially
15 carried out in the order mentioned.